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DEPARTMENT OF ENGINEERING

**nuclear hyperfine
structure of Mn^{++}**



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NUCLEAR HYPERFINE STRUCTURE OF Mn^{++}

HENDEL SACCO

The improvement of products which utilize phosphorescent materials, the materials which convert electrical energy into visible light, demand a more precise knowledge of the basic nature of phosphors. In this laboratory a detailed study of the magnetic properties of manganese activated phosphors is being made. It is the object of this report to give an interpretation to the experimental results obtained, in terms of the properties of the manganese ions used as activators in a variety of crystals.

DEPARTMENT OF ENGINEERING
UNIVERSITY OF CALIFORNIA
LOS ANGELES

FOREWORD

The research described in this report "Nuclear Hyperfine Structure of Mn^{++} " is part of a continuing program on Paramagnetism supported in part by the Office of Naval Research. The project is under the supervision of W. D. Hershberger in the Department of Engineering, University of California Los Angeles. L. M. K. Boelter is Chairman of the Department.

Mendel Sachs

Submitted in partial fulfillment of.

Contract No. N6-ONR 27519

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February 1953

ABSTRACT

A theoretical calculation of the nuclear hyperfine splitting in Mn^{++} is made by assuming that the ground state is composed of a mixture of the normal $3s^2 3d^5$ electronic configuration and a state created by the promotion of an inner 3s electron to the 4s state. Thus the ground state wave function is written as

$$\psi = \sqrt{1 - \alpha^2} \psi(3s^2 3d^5) + \alpha \psi(3s 3d^5 4s)$$

The numerical calculation of α is limited primarily by the inaccuracy of the value of the 3s and 4s radial wave functions at the nucleus. It is found that for the value $\alpha^2 \approx .14$, the observed hyperfine splitting is obtained.

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INTRODUCTION

The paramagnetic resonance spectra of Mn^{++} diluted in powdered samples of phosphor crystals has been observed in this laboratory.¹ The normal electronic configuration and ground state of Mn^{++} are $(1s)^2 \cdots (3s)^2 (3p)^6 (3d)^5$ and ${}^6S_{5/2}$ respectively. The nuclear hyperfine structure arises from an interaction between electronic and nuclear spins. This interaction is a function of $(3 \cos^2 \theta - 1)$. Since the normal configuration of Mn^{++} corresponds to a spherically symmetric charge distribution around the nucleus, the average value of $(3 \cos^2 \theta - 1)$ is zero, and there should be no observable hyperfine structure. It was pointed out by Abragam and Pryce² that a reduction of the spherical symmetry by a crystalline field would result in a very small splitting, and this splitting would show a characteristic anisotropy with respect to the direction of the external magnetic field. However, observations in this laboratory, and in many other laboratories, reveal a large isotropic splitting.

It has been suggested by Abragam and Pryce that the observed hyperfine structure may be due to an admixture to the normal electronic configuration of a configuration in which one of the inner electrons is promoted to a higher state. The unpaired electrons in the admixed state should then produce an isotropic hyperfine splitting.

Configurational coupling will only couple states with the same L , S , and parity³, so that the promoted state must also be a state with $L = 0$, $J = 5/2$ and $g = 2$. Abragam and Pryce suggest that the most probable promotion which will couple with the original 6S state is the promotion of a $3s$ electron to the $4s$ state. The wave function for the ground state of Mn^{++} may now be written as

$$(1) \quad \psi = \sqrt{1 - \alpha^2} \psi(3s^2 3d^5) + \alpha \psi(3s 3d^5 4s)$$

It is the purpose of this paper to calculate the fraction α which would account for the experimentally observed nuclear hyperfine splitting.

INTERACTION HAMILTONIAN

By means of an expansion of the electronic field into multipoles, it is found that the interaction energy between the electron cloud and the nuclear magnetic moment is $\mu_N \cdot H_0$, where H_0 is the magnetic field of the electron cloud at the nucleus, and μ_N is the magnetic moment of the nucleus. The vector potential of the electron cloud is $A = (\mu \times r)/r^3$ and the magnetic field is

$\mathbf{H} = \nabla \times \mathbf{A} = [3\mathbf{r}(\boldsymbol{\mu} \cdot \mathbf{r}) - \mu] r^{-3}$. The magnetic moment of the electron cloud is $\boldsymbol{\mu} = \mu(\mathbf{L} + 2\mathbf{S})$, and the nuclear magnetic moment is $\mu_N = \gamma \mu_N \mathbf{I}$.

The ground state of Mn^{++} has an orbital angular momentum $L = 0$, therefore our Hamiltonian operator is $\mathcal{H}_{hfs} = 2\gamma\mu_N\mu[3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - (\mathbf{S} \cdot \mathbf{I})]r^{-3}$.

If the unit vector \mathbf{r} is located at an angle (θ, ϕ) , then $[3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - (\mathbf{S} \cdot \mathbf{I})](m, m) = [S_z I_z (3 \cos^2 \theta - 1)](m, m)$, and the Hamiltonian is*

$$(2) \quad \mathcal{H}_{hfs} = 2\gamma\mu_N\mu S_z I_z (3 \cos^2 \theta - 1) r^{-3}$$

EIGENFUNCTIONS

The eigenfunctions for the $(3s3d^5 4s)$ wave function will be calculated by a method described by Gray and Wills.⁹ A review of this method will be given here.

The wave function for a seven electron system is written as

$$(3) \quad \Psi(m_{11}, m_{12}, m_{13}, m_{14}, m_{15}, m_{16}, m_{17}) = \psi(m_{11}, m_{12}) \psi(m_{13}, m_{14}) \cdots \psi(m_{15}, m_{16}, m_{17})$$

Making use of the general relation for any angular momentum operator \mathbf{J}

$$(4) \quad \hbar^{-1} (J_x - iJ_y) \psi(j, m) = [(j+m)(j-m+1)]^{\frac{1}{2}} \psi(j, m-1)$$

and calling $S_x - iS_y = \hat{S} = \hat{S}_1 + \hat{S}_2 + \cdots + \hat{S}_7$ we can write

$$(5) \quad \hat{S} \hbar^{-1} \psi(m_{11}, m_{12}, \cdots, m_{15}, m_{16}, m_{17}) = [(s_1 + m_{11})(s_1 - m_{11} + 1)]^{\frac{1}{2}} \psi(m_{11}, m_{12} - 1, m_{13}, m_{14}, \cdots) \\ + \cdots + [(s_7 + m_{17})(s_7 - m_{17} + 1)]^{\frac{1}{2}} \psi(m_{11}, m_{12}, \cdots, m_{16}, m_{17} - 1)$$

It is noted that

$$(6) \quad [(s + m_s)(s - m_s + 1)]^{\frac{1}{2}} = \delta(m_s, \pm \frac{1}{2})$$

Having found the eigenfunction $\Psi[L S M_L M_S]$ for $M_L = L$, $M_S = S$, this method provides a means of calculating the eigenfunctions for all other M_L and M_S values.

The following notation will be used:

$$\Psi[L S M_L M_S] = |^{S+1}L M_L M_S| \\ (m_{11}^{\pm}, m_{12}^{\pm}, \cdots, m_{17}^{\pm}) = \psi_1(m_{11}, m_{12} = \pm \frac{1}{2}) \psi_2(m_{13}, m_{14} = \pm \frac{1}{2}) \cdots \psi_7(m_{15}, m_{16} = \pm \frac{1}{2})$$

Since we are interested in an S state, the eigenfunctions desired are $[^4S 0 \pm \frac{1}{2}]$, $[^4S 0 \pm \frac{1}{2}]$, and $[^4S 0 \pm \frac{1}{2}]$.

CALCULATION OF THE $(^4S 0 \frac{1}{2})$ STATE

For the $3s 3d^4 4s$ configuration the eigenfunction for the $M_J = J$ state is

$$(^4S 0 \frac{1}{2}) = 2^{-\frac{1}{2}} [(0^+ 0^-) - (0^- 0^+)] (2^+ -2^+ 1^+ -1^+ 0^+)$$

The first bracket represents the antisymmetrized wave function for the two non-equivalent s electrons, the second bracket is the $3d^4$ part of the wave function.

Using the relation (4) we have:

$$(7) \quad \delta[^4S 0 \frac{1}{2}] = 5^{-\frac{1}{2}} [^4S 0 \frac{1}{2}]$$

Using relation (5) we have:

$$(8) \quad \delta[^4S 0 \frac{1}{2}] = 2^{-\frac{1}{2}} [(0^+ 0^-) - (0^- 0^+)] \{ (2^+ -2^+ 1^+ -1^+ 0^+) + (2^+ -2^+ 1^+ -1^+ 0^+) + (2^+ -2^+ 1^+ -1^+ 0^+) + (2^+ -2^+ 1^+ -1^+ 0^+) + (2^+ -2^+ 1^+ -1^+ 0^+) \}$$

Equating expressions (7) and (8) we have.

$$(9) \quad [^4S 0 + \frac{1}{2}] = 10^{-\frac{1}{2}} [(0^+ 0^-) - (0^- 0^+)] \sum_{i=1}^5 x_i^+$$

The eigenfunctions x_i^+ are written down explicitly in Appendix II.

In a similar fashion we obtain

$$(10) \quad [^4S 0 + \frac{1}{2}] = 20^{-\frac{1}{2}} [(0^+ 0^-) - (0^- 0^+)] \sum_{i=1}^{10} y_i^+$$

$$(11) \quad [^4S 0 - \frac{1}{2}] = 20^{-\frac{1}{2}} [(0^+ 0^-) - (0^- 0^+)] \sum_{i=1}^{10} y_i^-$$

MATRIX ELEMENTS

We will now calculate the matrix elements $(L S J M | \mathcal{H} | L S J M)$ where the Hamiltonian is given in equation (2). In terms of the ground state wave function (1) the energy eigenvalue \mathcal{H} is

$$\mathcal{H} = (\sqrt{1-\alpha^2} \psi[3s^2 3d^4] + \alpha \psi[3s 3d^4 4s]) | \mathcal{H} | (\sqrt{1-\alpha^2} \psi[3s^2 3d^4] + \alpha \psi[3s 3d^4 4s])$$

Since $(\psi[3s^2 3d^4] | \mathcal{H} | \psi[3s^2 3d^4]) = 0$ and $(\psi[3s^2 3d^4] | \mathcal{H} | \psi[3s 3d^4 4s]) = 0$.

then $\mathcal{H}' = \alpha^2 (\psi[3s 3d^4 4s] | \mathcal{H} | \psi[3s 3d^4 4s])$, or

$$(12) \quad \mathcal{H}'_{H, J} = 2\alpha^2 \gamma \mu_N \mu (m | I_z | m) \left([{}^6S 0 M] \left| \frac{S_z (3 \cos^2 \theta - 1)}{r^3} \right| [{}^6S 0 M] \right)$$

Since we are dealing with an S state $M_J = M_L$ and the eigenfunctions in the $M_L M_S$ system are identical with the eigenfunctions in the MJ system.

The spin operator only affects the spins of the individual electrons, and the $(3 \cos^2 \theta - 1)$ operator only affects the m_l values, hence the spin orbital and radial parts are treated separately.

Recalling that the interaction between the magnetic field due to the electron cloud and the nuclear moment takes place at the nucleus, and that the $3s$ and $4s$ unpaired electrons are the cause of the splitting, we can write

$$(13) \quad ([{}^6S 0 M] | S_z (3 \cos^2 \theta - 1) r^{-3} | [{}^6S 0 M]) \\ = ([{}^6S 0 M] | S_z (3 \cos^2 \theta - 1) | [{}^6S 0 M]) (R_{3s}(1) R_{4s}(1) \\ + R_{3s}(2) R_{4s}(1) | r_1^{-3} + r_2^{-3} | R_{3s}(1) R_{4s}(2) + R_{3s}(2) R_{4s}(1)) = 4(\theta, \phi) \mathcal{R}(r)$$

where $A(\theta, \phi)$ is the angular part of the integral, $\mathcal{R}(r)$ is the radial part of the integral, and where 1 and 2 represent the two spatial points (x_1, y_1, z_1) and (x_2, y_2, z_2) .

It turns out that $\mathcal{R}(r) = 2(R_{3s}^2(0) + R_{4s}^2(0))$.^{*} Hence

$$(14) \quad \mathcal{H}'_{H, J} = 4\alpha^2 \gamma \mu_N \mu (R_{3s}^2(0) + R_{4s}^2(0)) ([{}^6S 0 M] | S_z (3 \cos^2 \theta - 1) | [{}^6S 0 M])$$

CALCULATION OF $([{}^6S 0 M] | S_z (3 \cos^2 \theta - 1) | [{}^6S 0 M])$

1. When we operate on the wave function $({}^6S 0 M)$ with $S_z = s_{z1} + s_{z2} + \dots + s_{iz}$, we obtain

$$(15a) \quad S_z [{}^6S 0 \pm \frac{1}{2}] = \frac{5}{\sqrt{2}} [(0^+ 0^-) - (0^- 0^+)] (2^{\pm} - 2^{\pm} 1^{\pm} - 1^{\pm} 0^{\pm})$$

$$(15b) \quad S_z [{}^6S 0 \pm \frac{1}{2}] = \frac{3}{\sqrt{2}} \left[\sum_{i=1}^5 x_i^2 \right] [(0^+ 0^-) - (0^- 0^+)]$$

$$(15c) \quad S_z [{}^6S 0 \pm \frac{1}{2}] = \frac{1}{\sqrt{2}} \left[\sum_{i=1}^{10} y_i^2 \right] [(0^+ 0^-) - (0^- 0^+)]$$

^{*} Appendix III

Hence we have for $M = 1/2$

$$(16) \quad ([^6S \ 0 \ 1/2] | S_z (3 \cos^2 \theta - 1) | [^6S \ 0 \ 1/2]) = \\ \frac{1}{2} [(0^+ 0^+) - (0^- 0^-)] (2^+ - 2^+ 1^+ - 1^+ 0^+) | (3 \cos^2 \theta - 1) | [(0^+ 0^+) - (0^- 0^-)] (2^+ - 2^+ 1^+ - 1^+ 0^+)$$

2. Operation with $(3 \cos^2 \theta - 1)$.

In Appendix II it is shown that

$$(17) \quad (3 \cos^2 \theta - 1) = \frac{3}{S(S+1)} [j_1(j_1+1) \cos^2 \theta_1 + \dots + j_l(j_l+1) \cos^2 \theta_l - \frac{1}{2} S(S+1)]$$

plus terms whose matrix elements vanish.

The values of $j(j+1) \cos^2 \theta (m, m)$ for $l = 2 \ m = 2 \dots -2$ and $l = m = 0$ are shown in the following table.*

l	m	$j(j+1) \cos^2 \theta (m, m)$
2	± 2	27/28
2	± 1	81/28
2	0	99/28
0	0	7/28

Hence from equations (15) and (16) we have

$$([^6S \ 0 \ 1/2] | S_z (3 \cos^2 \theta - 1) | [^6S \ 0 \ 1/2]) = \frac{(1039)(6)}{(49)(35)}$$

and

$$(18a) \quad \chi_{1/2, \pm} = \frac{24936}{1715} \alpha^2 \gamma \mu_N \mu [R_{3,1}^2(0) + R_{4,1}^2(0)] \pi + \frac{1}{2} g \mu H$$

$$(18b) \quad \chi_{1/2, \pm} = \frac{3}{5} \chi_{1/2, \pm}$$

$$(18c) \quad \chi_{1/2, \pm} = \frac{1}{5} \chi_{1/2, \pm}$$

The selection rules for paramagnetic resonance absorption are $\Delta M = \pm 1$, $\Delta m = 0$. Therefore, the transition energy is

$$(19) \quad (h\nu)_{\pm} = \chi_{1/2, \pm} - \chi_{1/2, \pm} = 5.814 \alpha^2 \gamma \mu_N \mu [R_{3,1}^2(0) + R_{4,1}^2(0)] \pi + g \mu H$$

The hyperfine splitting constant is equal to

$$A = \frac{(h\nu)_{\pm} - (h\nu)_{\pm 1}}{g \mu} = 2.907 \alpha^2 \gamma \mu_N \mu [R_{3,1}^2(0) + R_{4,1}^2(0)] \text{ gauss}$$

* Appendix V.

NUMERICAL CALCULATIONS

The value of α can now be computed from the values of A obtained by Hershberger and Leifer.¹

We shall assume Hydrogenic wave functions with an effective charge $Z_{n,l}$.² The value of $Z_{n,l}$ is estimated by subtracting the electronic charge under the n,l shell from the nuclear charge.

Using the values

$$a = 5.28 \times 10^{-9} \text{ cm}$$

$$\mu_N = 5.05 \times 10^{-24} \text{ erg gauss}^{-1}$$

$$\gamma = 3.47$$

$$Z_{3,0} = 15$$

$$Z_{4,0} = 3$$

$$A = 76.2 \text{ gauss}$$

we obtain

$$\alpha^2 = .143.$$

CONCLUSIONS

Due to the inaccuracy with which the effective charge $Z_{n,l}$ was estimated, the numerical calculation given here merely gives an order of magnitude for α .

This laboratory is now making use of the proton resonance method of measuring magnetic fields. It has also been brought to my attention that a program of evaluating $R_{n,l}$ for many electron atoms is now under way at M.I.T.³ If the radial wave function for Mn^{++} becomes available, then together with the more accurate field measurement a much more accurate estimation of α can be made.

Assuming that the theory of the mixture of states is the reason for the large nuclear hyperfine splitting of Mn^{++} , it is fairly safe to say that the ground state wave function for Mn^{++} is

$$\psi_0 = \sqrt{.86} \psi(3s^2 3d^1) + \sqrt{.14} \psi(3s 3d^1 4s).$$

$$R_{n,l}(r) = \left[\left(\frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} e^{-Zr/na} \rho^l L_{n-l-1}^{2l+1}$$

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APPENDIX I

If the vectors I , S , and r are at the angles (θ_1, ϕ_1) , (θ_2, ϕ_2) , and (θ, ϕ) , respectively, then the quantity

$$3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - \mathbf{S} \cdot \mathbf{I} =$$

$$\begin{aligned} & SI \{ (3 \cos^2 \theta - 1) \cos \theta_1 \cos \theta_2 + (3 \sin^2 \theta - 1) [\cos^2 \theta \sin \theta_1 \sin \theta_2 \cos(\phi_1 + \phi_2) \\ & + \cos \phi \sin \phi \sin \theta_1 \sin \theta_2 \sin(\phi_1 + \phi_2) - \cos \phi_1 \cos \phi_2] \\ & + 3 \sin \theta \cos \theta (\cos \phi (\sin \theta_1 \cos \theta_2 \cos \phi_1 + \sin \theta_2 \cos \theta_1 \cos \phi_2) \\ & + \sin \phi (\sin \theta_1 \cos \theta_2 \sin \phi_1 + \sin \theta_2 \cos \theta_1 \sin \phi_2)) \} \end{aligned}$$

The selection rules for transitions between nuclear π levels is $\Delta\pi = 0$. Therefore, due to parity considerations the diagonal matrix elements of all terms involving $\sin \phi$ or $\cos \phi$ vanish. Hence our Hamiltonian operator becomes

$$H_{\text{h.f.}} = S \cdot I + (3 \cos^2 \theta - 1) r^2$$

APPENDIX II

$$x_1^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$x_2^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$x_3^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$x_4^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$x_5^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_1^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_2^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_3^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_4^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_5^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_6^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_7^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_8^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_9^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$y_{10}^{\pm} = (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$(\pm S \ 0 \ \pm 1/2) = 2 * [(0^+ \ 0^-) - (0^- \ 0^+)] (2^{\pm} - 2^{\pm} \ 1^{\pm} - 1^{\pm} \ 0^{\pm})$$

$$(\pm S \ 0 \ \pm 1/2) = 10 * [(0^+ \ 0^-) - (0^- \ 0^+)] \sum_{i=1}^5 x_i^{\pm}$$

$$(\pm S \ 0 \ \pm 1/2) = 20 * [(0^+ \ 0^-) - (0^- \ 0^+)] \sum_{i=1}^{10} y_i^{\pm}$$

APPENDIX III

EVALUATION OF THE r^{-3} PART OF THE MATRIX ELEMENT

$$\begin{aligned}
 R(r) &= ([R_{3a}(1)R_{4a}(2) - R_{3a}(2)R_{4a}(1)] | r_1^{-3} + r_2^{-3} | [R_{3a}(1)R_{4a}(2) - R_{3a}(2)R_{4a}(1)]) \\
 &= 2(R_{3a} | r^{-3} | R_{3a})(R_{4a} | R_{4a}) + 2(R_{3a} | R_{3a})(R_{4a} | r^{-3} | R_{4a}) \\
 &\quad + \text{additional terms which vanish because of orthogonality.}
 \end{aligned}$$

Using Fermi's result for s electrons it is found that

$$R = 2[R_{3a}^2(0) + R_{4a}^2(0)]$$

APPENDIX IV

Using the vector model of the atom we have:

$$\begin{aligned}
 [J(J+1)]^{\frac{1}{2}} \cos \theta &= [j_1(j_1+1)]^{\frac{1}{2}} \cos \theta_1 + \cdots + [j_2(j_2+1)]^{\frac{1}{2}} \cos \theta_2, \\
 [J(J+1)] \cos^2 \theta &= j_1(j_1+1) \cos^2 \theta_1 + \cdots + j_2(j_2+1) \cos^2 \theta_2 \\
 &\quad + [j_1 j_2 (j_1+1)(j_2+1)]^{\frac{1}{2}} \cos \theta_1 \cos \theta_2 + \cdots
 \end{aligned}$$

The cross product terms give a zero diagonal matrix element because of the odd parity of $\cos \theta$. Since $J = S$ we have

$$\begin{aligned}
 (3 \cos^2 \theta - 1) &= \frac{3}{S(S+1)} [j_1(j_1+1) \cos^2 \theta_1 + \cdots + j_2(j_2+1) \cos^2 \theta_2 \\
 &\quad - \frac{1}{3} S(S+1)]
 \end{aligned}$$

APPENDIX V

$$\begin{aligned}
 (1) \quad (j \ m | \cos^2 \theta | j \ m) &= \sum_{m_1} (j \ m | m_1 \ m_1) (m_1 \ m_1 | \cos^2 \theta | m_1 \ m_1 | j \ m) \delta(m, m_1 + m_1) \\
 &= (j \ m | m_1 \ 1/2) (m_1 \ 1/2 | \cos^2 \theta | m_1 \ 1/2) (m_1 \ 1/2 | j \ m) + (j \ m | m_1 \ -1/2) (m_1 \ -1/2 | \cos^2 \theta | m_1 \ -1/2) (m_1 \ -1/2 | j \ m)
 \end{aligned}$$

$$(2) \quad (m_1 \ m_1 | \cos^2 \theta | m_1 \ m_1) = \int_{-1}^1 P_l^m(\cos \theta) \cos^2 \theta P_l^m(\cos \theta) d(\cos \theta) = \frac{2(l^2 - m_1^2) + (2l - 1)}{(2l + 3)(2l - 1)}$$

$(j \ m | m_1 \ m_1)$ is a matrix element of the Rotation Group (Wigner coefficient) and has the values

$$(3) \quad (j \ m | m_1 \ m_1) = \begin{array}{c|cc} & +1/2 & -1/2 \\ \hline j \backslash m_1 & & \\ \hline l + 1/2 & \left(\frac{l + m_1 + 1}{2l + 1} \right)^x & \left(\frac{l - m_1 + 1}{2l + 1} \right)^x \\ \hline l - 1/2 & - \left(\frac{l - m_1}{2l + 1} \right)^x & \left(\frac{l + m_1}{2l + 1} \right)^x \end{array}$$

Since we do not know whether $j = l + 1/2$ or $j = l - 1/2$, we shall assume that both states are equally probable. The matrix element is therefore averaged over both states of the electron.

From equations (1), (2) and (3) we have

$$\begin{aligned}
 &\overline{j(j+1) \cos^2 \theta(m, m)} = \\
 &\frac{(l + 1/2)(l + 1/2)(l + 1)[2(l - m_1)(l + m_1) + (2l - 1)] + (l - 1/2)(l + 1/2)l[2(l - m_1)(l + m_1) + (2l - 1)]}{(2l + 3)(2l - 1)(2l + 1)} \\
 (4) \quad &\overline{j(j+1) \cos^2 \theta(m, m)} = \frac{[2(l + m_1)(l - m_1) + (2l - 1)][4l(l + 1) + 3]}{4(2l + 3)(2l - 1)}
 \end{aligned}$$

The values in the table (p. 5) were calculated with equation (4).

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